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The Growth of Bamboo-Structured Carbon Tubes Using a Copper Catalyst

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ABSTRACT

Catalytic decomposition of methane has been used to grow bamboo-structured carbon tubes at temperatures ranging from 1233 K to 1291 K. No tube growth was observed at temperatures less than 1233 K, whilst above 1291 K pyrocarbon was the dominant product. It is shown that the average size of the copper catalyst particles was influenced by the reaction temperature, with the reciprocal of the maximum size of the copper particle decreasing linearly with temperature. This is consistent with the idea that the melting point can be reduced by surface energy effects. Observations show that under the conditions here the catalyst particle penetrates into the carbon fibre and a mechanism is proposed for development of the bamboo structure based upon the energy changes that take place.

INTRODUCTION

A wide range of carbon structures can be formed by the catalytic decomposition of hydrocarbons or the disproportionation of CO including various types of tubes and fibres as well as shells and stacks. In this paper hollow carbon fibres grown from copper catalyst particles are described. The most striking feature of these bamboo fibres is the repeating nature of the structure due to the formation of a transverse wall of carbon across the tube at regular intervals. Several authors have suggested that this structure might involve capillary forces causing the liquid or solid metal catalyst to move suddenly up the carbon tube [1-5], although the detailed mechanism is not understood. In this paper we describe some experiments using a copper catalyst and how capillary forces may give rise to such a sudden movement of the liquid catalyst enabling the bamboo structure to form.

EXPERIMENTAL DETAILS

A copper catalyst was produced by precipitation from a solution of hydrated copper nitrate, $Cu(NO_3)_2 \cdot 3H_2O$, and ammonium hydrogen carbonate, NH_4HCO_3. The precipitate was removed using a centrifuge and dried at 378 K for 12 hours. The resulting particles were then ground with a pestle and mortar before placing a small quantity on an alumina substrate. This was placed in a tube furnace and calcined at 673 K in air for 4 hours before purging with Ar then H_2. The furnace was then heated to the desired reaction temperature. At 25 K below the final temperature CH_4 was introduced. The flow rates for H_2 (99.995% pure) and CH_4 (99.999% pure) were 1.4 l min^{-1} and 0.2 l min^{-1} respectively through a tube with a 60 mm internal diameter. The tube was held at constant temperature for 1 hour and then cooled under flowing Ar. The carbon grown was examined using a Jeol JSM-6340F field emission scanning electron microscope (SEM) and a Jeol JSM 2000FX transmission electron microscope (TEM). For SEM the samples were examined directly and for TEM the carbon products were scraped off the substrates on to gold supported amorphous carbon grids.

RESULTS AND DISCUSSION

Carbon fibres only grew at temperatures between 1233 K and 1291 K. At high reaction temperatures pyrocarbon formed, whilst below 1233 K no reaction occurred. Within this temperature range the lengths of the fibres after 1 hour were approximately 2 μm at 1233 K, but were many hundreds of micrometers at 1291 K. However the most striking feature of the fibres that formed was that they had walls lying perpendicular to the direction of growth forming a regular cell structure which can be seen in figure 1(a). At a given temperature, the shape of the segments and the segment aspect ratio was independent of fibre diameter.

The copper catalyst particles could be seen at the ends of the fibre, as can be seen in detail in figure 1(b). The catalyst particles have a diameter larger than the fibre with which they are associated and there is a fixed ratio between the catalyst particle diameter and the fibre diameter, see figure 2.

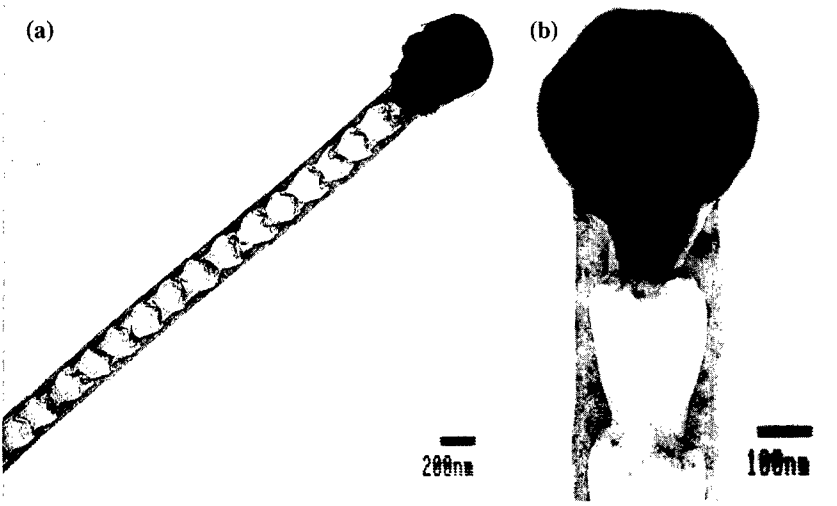

Figure 1(a). A TEM micrograph of a bamboo fibre grown at 1278 K showing the repeating internal structure and a copper catalyst particle at the tip. **Figure 1(b).** A TEM micrograph showing a catalyst particle with a conical shaped tail sat inside a conical carbon cell grown at 1278 K.

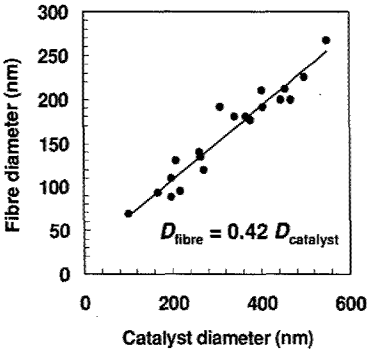

Figure 2. The variation of the fibre diameter with the diameter of the catalyst particle for fibres grown at 1278 K.

The maximum size of the catalyst particles that were observed increased with increasing temperature as shown in figure 3. Extrapolating the experimental data gives an intercept on the abscissa of 1356 K compared with the bulk melting temperature of copper of 1357 K. These observations are consistent with the idea that the catalyst particles are molten at the reaction temperature, where the suppression in melting point being associated with effects due to surface tension.

Increasing the reaction temperature decreases the diameter of the fibre that forms on a given volume of catalyst particle, the fibre size being approximately 0.64 of the catalyst particle diameter at 1233 K but only 0.42 of the catalyst particle diameter at 1291 K.

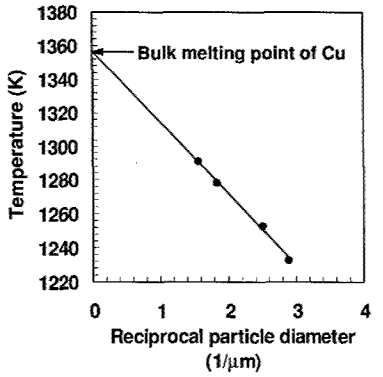

Figure 3. A plot of the maximum observed catalyst particle diameters over a range of temperatures plotted as a reciprocal versus temperature. The line of best fit intercepts the abscissa at a temperature of 1356 K, close to the bulk melting temperature of pure copper of 1357 K.

Figure 1(b) shows that the catalyst particle does not just sit as a spherical particle on top of the fibre, but has a 'tail' that penetrates into the cell structure. The surface area of the overall particle is therefore slightly greater than it would have been if it had remained completely spherical. This can only occur if there is a reduction in the energy of the surfaces of the particle that is when

$$\Delta A_{\text{particle}}\gamma_{Cu/g} + \Delta A_{\text{tail}}\left(\gamma_{Cu/C} - \gamma_{C/g}\right) \leq 0 \qquad (1)$$

where $\gamma_{Cu/g}$ is the energy of the interface between copper and the gaseous environment, $\gamma_{C/g}$ is the energy of the interface between carbon fibre and the gaseous environment, $\gamma_{Cu/C}$ is the energy of the surface between copper and carbon, $\Delta A_{\text{particle}}$ is the change in area of the spherical portion of the particle and ΔA_{tail} is the area of the surface of the tail that was formed within the tube.

From the above expression three types of behaviour are evident. Where $\gamma_{Cu/g} < (\gamma_{Cu/C} - \gamma_{C/g})$, the catalyst will form a spherical particle at the end of the fibre. If instead $\gamma_{Cu/g} >> (\gamma_{Cu/C} - \gamma_{C/g})$ the catalyst will be contained entirely within the carbon tube. There is also an intermediate range of surface energies where equation 1 is obeyed, when the liquid flowing into the tube causes an initial reduction in the energy of the system as the reduction in surface energy outweighs the increase in surface area. However, as the liquid extends further into the narrowing tube, the increase in surface area eventually outweighs the change in surface energies, giving a curve as shown in figure 5, so that a tail of equilibrium length, l_e, is predicted to form. The extent of this penetration depends on the relative surface energies and on the internal shape of the tube.

Simply allowing the catalyst particle with its tail of equilibrium length to move upward at a constant rate would not give the observed cell structure, but rather a solid fibre or possibly an empty tube. The formation of the cell structure in these fibres would seem to require that the tail expanded and contracted whilst the carbon fibre was growing.

One might therefore consider a possible mechanism for the formation of the bamboo structure as follows. Consider a growing carbon tube containing truncated conical cells, as observed in figure 1(b), with a catalyst particle on top and with the surface energies such that a tail of an equilibrium length, l_e, is formed at time t_0, as shown in figure 5. The transverse wall can form by the precipitation of carbon on the underside of the drop at t_1 as shown in figure 6, lowering the overall energy of the system from its initial value at t_0. By t_2 further precipitation causes lengthening of the tube whilst also reducing the internal dimensions elongating the metal particle so that the overall energy of the surfaces further increases.

Eventually the increase in the energy of the surfaces caused by this growth of the tube and reduction of the internal dimension is such that it becomes energetically favourable for the tail to reform and the process begins again. This overall process allows the formation of the transverse wall and for the liquid adjacent to it to move rapidly up the tube giving a repeating process.

All of the changes in the energy of the surfaces are measured from the situation where the catalyst particle sits on top of the carbon tube as a sphere.

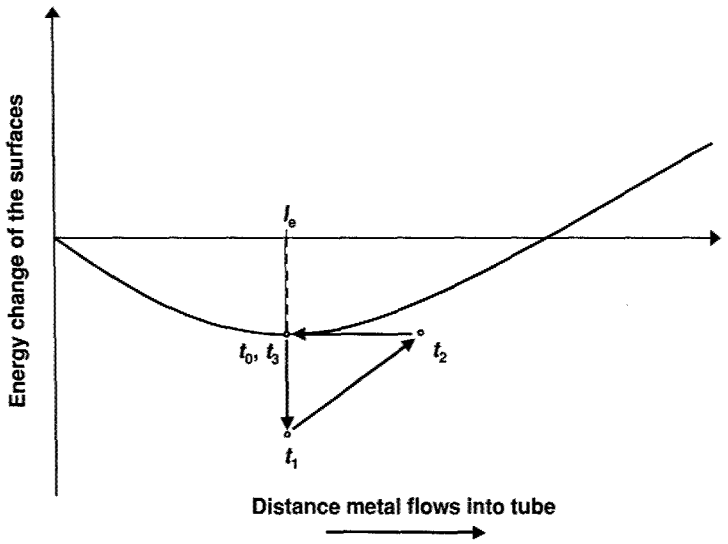

Figure 5. The change in energy of the surfaces during the steps shown in figure 6. The curve shows the energy change that occurs when the liquid catalyst flows into the initial carbon cone. The energy and position of the initial equilibrium tail formed is at t_0. This energy is reduced by the precipitation of the transverse wall at t_1. Further precipitation causes the dimensions of the drop to change until eventually the energy of the surfaces is equal to that at t_0, whereupon the liquid moves rapidly up the tube. The position of zero energy change is where the droplet forms a sphere on top of the fibre.

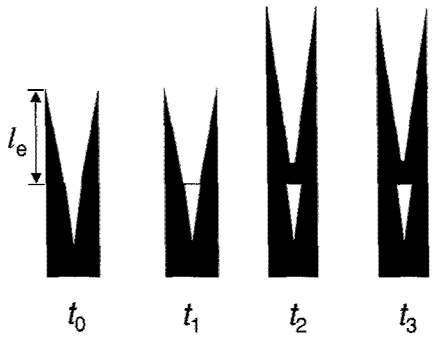

Figure 6. A schematic representation of a sequence of events during the growth of a bamboo carbon fibre.

The process shown in figure 5 illustrates a particular case where the new tail formed is of the same dimension as that of the original one and the growth process is therefore at a steady-state. If the initial conditions are that steady-state growth does not occur immediately, it is found that the cell changes shape until a steady-state is reached. For a fixed catalyst volume and fibre diameter, the cell shape produced during steady state growth is dependent on the ratios of the surface energies and the rate at which the tube lengthens compared with the rate at which the internal dimensions decrease, and it is independent of the shape of starting cone used.

This repeating process will only work within certain limits of surface energies, tube dimensions and geometries. For instance, the process can break down if the rate at which the tube lengthens compared with the rate at which the internal dimensions decrease is very high. When this occurs the energy of the system at t_2 is never greater than the energy at t_3 and there is no driving force for the catalyst to move from the position at t_0 to that at t_3, so that the catalyst particle will tend to completely envelope within the tube. Also, if the internal dimensions are very small, the energy changes required to form a tail are much greater, so that solid fibres and tubes tend to form instead. This is consistent with observations elsewhere[3].

CONCLUSIONS

The growth of hollow bamboo fibres using a copper catalyst in CH_4 and H_2 gas at temperatures in the range 1233 to 1291 K has been studied. Observation of the size of the largest observed catalyst particle suggests that the copper is molten during fibre growth. A model based upon changes of the energies of the surface has been proposed which gives a mechanism for the formation of bamboo-structured carbon fibres and which also shows that transitions to tubes and fibres can be easily obtained.

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